

# PATENT SPECIFICATION

NO DRAWINGS

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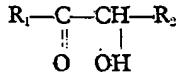
## COMPLETE SPECIFICATION

### Purification of Phenol

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Tcrphichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent 5 may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the 10 purification of phenol, and in particular to the purification of phenol derived from cumene.

Phenol derived from cumene contains impurities which cause the development of an 15 undesired colour when the phenol is subjected to chlorination or sulphonation, such impurities including aliphatic  $\alpha$ -hydroxy carbonyl compounds of the formula



20 These  $\alpha$ -hydroxy carbonyl compounds may condense with phenol to form benzofurans, and such benzofurans are responsible, at least in part, for the formation of the coloured compounds when the phenol containing them 25 is subjected to chlorination or sulphonation. They are thus undesirable constituents of the product phenol, and may be formed at any time by condensation of the  $\alpha$ -hydroxy carbonyl compounds referred to above with the 30 phenol, when the phenol is heated, especially in the presence of substances which catalyse the condensation. The  $\alpha$ -hydroxy carbonyl compounds are not readily separable from 35 compounds are not readily separable from furans may be separated therefrom substantially completely, for example by extractive distillation.

It has previously been proposed to purify 40 phenol containing benzofurans and their precursors by heating the phenol in the presence of specified catalysts to promote reaction between phenol and the  $\alpha$ -hydroxy carbonyl compounds, and to remove the benzofurans

formed, for example, by extractive distillation in the presence of water.

This process depends upon substantially 45 complete reaction of the benzofuran precursors with phenol, followed by substantially complete separation of the benzofurans from the phenol.

According to the present invention, the process for the purification of phenol derived 50 from cumene comprises subjecting the impure phenol to fractional distillation to remove acetone, heating the substantially acetone-free phenol-containing material under acid conditions with an acidic catalyst until the benzofuran content of the reaction mixture has been reduced to a practical minimum, and subjecting the reaction mixture to fractional distillation to recover a purified phenol-containing material.

The process of the invention is carried out 55 on phenol which is substantially acetone-free and may contain other impurities boiling lower than phenol and/or impurities boiling higher than phenol. The phenol used as starting material may, however, be subjected to fractional distillation to remove both high-boiling and low-boiling impurities before being treated by the process of the present invention.

In the process of this invention, the benzofuran precursors are condensed with phenol 60 to produce benzofurans, which are then converted to other products which may be separated from the phenol by ordinary fractional distillation. In the process, the benzofurans may be decomposed or may undergo further condensation reactions whereby they are converted to materials readily separable from phenol.

Suitable catalysts for use in the process of 65 this invention include mineral acids, such as sulphuric acid and phosphoric acid, strong organic acids such as p-toluene sulphonic acid, benzene sulphonic acid and trichloracetic acid, acidic clays such as an acid-treated bentonite

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or a naturally occurring acidic clay, and acidic ion exchange resins such as sulphonated styrene-divinyl benzene resin. Other suitable catalysts are boron trifluoride and the halides, 5 sulphates and nitrates of copper, chromium, mercury, platinum, zinc, cadmium, gallium, vanadium and the metals of Groups IV and VIII of the Periodic Table having an atomic number less than 52. Of the metallic compounds, 10 the preferred catalysts are those of the Friedel-Crafts type which include aluminium chloride, aluminium bromide, antimony pentachloride, antimony trichloride, ferric chloride, stannic chloride, titanium trichloride, 15 titanium tetrachloride, zirconium chloride and zinc chloride.

The amount of catalyst used in the process of the present invention may vary within moderately wide limits, but will generally be 20 within the range 0.005% to 5% by weight based on the weight of the phenol-containing material to be treated. A preferred range is from 0.1% to 1% by weight. The activity of 25 the catalyst will, to a certain extent, determine the amount to be used. Larger amounts of less active catalysts will be needed, particularly when it is desired to keep the reaction period as short as possible. The catalytic treatment 30 is carried out for the length of time required to reach a practical minimum content of benzofurans, as determined by analysis.

The temperature at which the process takes place will lie within the range in which phenol is liquid under the conditions of the 35 reaction, and will thus be between 40° C. and 182° C. at atmospheric pressure. Pressures higher or lower than atmospheric may be used; higher pressures may be advantageous, since it is then possible to employ 40 higher temperatures. A preferred temperature range is between 150° C. and the boiling point of phenol at the operating pressure.

During the reaction period it is desirable 45 to have as little water present as is practical. Otherwise, it may be necessary to use a greater amount of catalyst than would be required under substantially anhydrous conditions, since water tends to decrease the activity of the catalysts. Thus, for example, 50 boron trifluoride and aluminium chloride require anhydrous conditions. Others however, such as ferric chloride, ferric sulphate and sulphuric acid, are quite satisfactory in their activity with up to 15% by weight of water 55 present, based on the weight of the phenol containing material being treated.

After treatment of the phenol-containing material by the process of this invention, it 60 is fractionally distilled to recover a purified material. In this distillation the products of conversion of the benzofurans are separated. Some of these boil at temperatures lower than phenol, and some boil at temperatures higher than phenol. Other impurities which remain

in the phenol may be removed in the same 65 distillation.

While the process of the present invention may be employed alone for the removal of benzofurans and their precursors, it may also be applied to phenol which has already been 70 treated by the process of the invention described and claimed in British Patent Application Serial Number 883,746. In this process, the phenol is treated with a base in the liquid phase for at least 15 minutes at a 75 temperature between 20° C. and 250° C.; the pH value of the phenol is preferably in the range 6.0 to 8.5 during the treatment. The product phenol is fractionally distilled, and the phenol fraction is used as the starting material in the process of the present invention.

The following examples further illustrate the invention. In the examples, the following colour test was employed to investigate the colour formed when the phenol was chlorinated.

10±0.1 g. of the phenol to be tested was placed in a 25 mm. test tube fitted with a gas inlet tube extending to the bottom of the test tube, a gas outlet tube and a stopper. Chlorine gas was passed through the phenol at a rate of one litre per minute, the phenol by ordinary methods, but the benzene by cooling the vessel. The chlorination was stopped when the weight of the phenol had increased by 5.5-6.0 grams. The chlorinated product was transferred to a 1 cm. cell and analysed in a recording spectrophotometer. The absorption at 510 and 540 m $\mu$  was noted, and also the position of maximum absorption. The absorbance is a measure of the intensity of absorption, and is defined as the logarithm of the reciprocal of the transmittance.

#### EXAMPLE 1

Cumene was oxidised to the hydroperoxide and the hydroperoxide was subjected to acid cleavage. The acid catalyst in the cleavage mixture was removed by extraction with a concentrated aqueous solution of sodium sulphate. The extracted cleavage mixture was subjected to fractional distillation in a series of columns. In the first column acetone was taken off overhead, leaving as base product a mixture of phenol, some cumene and  $\alpha$ -methylstyrene, and high-boiling material composed primarily of acetophenone, phenyl-dimethyl carbinol and cumylphenol. This base product was separated in the next column into an overhead crude phenol fraction and a high-boiling residue. The crude phenol fraction was subjected to steam distillation in a third column to remove overhead azeotropes of water with cumene and  $\alpha$ -methylstyrene, and to recover a base product consisting substantially of phenol.

This base product phenol, containing 41

parts per million of 2-methylbenzofuran (2-MBF) as determined by ultraviolet analysis, was stored in a steel container. Batch distillation of the stored material gave a product 5 phenol containing 1345 p.p.m. 2-MBF, formed as a result of reaction between the phenol and 2-MBF precursors during storage and subsequent distillation.

10 1% by weight of ferric chloride was added to the distilled, stored product phenol and the resulting mixture was heated at a reflux temperature of 175°—180° C. for 20 hours, at which time an additional 0.5% by weight of ferric chloride was added. The heating 15 was continued for a total of 33 hours. During the first three hours of treatment, the 2-MBF content decreased from the initial 1345 p.p.m. to 113 p.p.m. After 11 hours the 2-MBF content was 68 p.p.m. and after 20 hours 20 50 p.p.m. At the end of 23 hours there was less than 30 p.p.m. 2-MBF in the mixture.

Upon completion of the reaction after 33 25 hours, the phenol was fractionally distilled under a pressure of 400 mm Hg. The various cuts taken ranged from zero to seven parts per million of 2-MBF, and the average for all cuts was four parts per million.

The distilled phenol was chlorinated as 30 described above, and the colour produced was 0.2 absorbance units at 540 m $\mu$ .

#### EXAMPLE 2

A product phenol similar to that obtained in Example 1 by batch distillation of stored material, but containing 915 p.p.m. 2-MBF, 35 was heated at 120° C. in the presence of 0.5% ferric chloride. After 71 hours the 2-MBF content of the reaction mixture was 34 p.p.m. Fractional distillation gave a product having a chlorination colour of 1.64 absorbance units at 540 m $\mu$ .

#### EXAMPLE 3

A product phenol similar to that described in Example 1 but containing 770 p.p.m. 2-MBF was used in a series of runs involving several different catalytic materials. 45 In all instances the phenol was heated at 180° C. in the presence of the specified amount of catalyst. With 1% by weight of concentrated sulphuric acid, the 2-MBF content was 183 p.p.m. after 18 hours, and after 50 24 hours no 2-MBF was detected. Cupric sulphate, 1.2% by weight, resulted in a decrease to 105 p.p.m. 2-MBF after 66 hours. With 1.2% by weight of aluminium chloride 55 the amount of 2-MBF was 91 p.p.m. after 49 hours. Fractional distillation of the phenol treated with sulphuric acid gave a product which was completely satisfactory with respect to colour on chlorination. The other two phenols required additional catalytic treatment 60 before acceptable products were obtained by distillation.

#### EXAMPLE 4

Catalytic treatments comparable to those in Example 4 except for the use of chromic chloride, mercuric chloride, an acid-treated bentonite and p-toluene sulphonic acid as catalysts all resulted in a decrease in 2-MBF content in the reaction mixture. The time required for each catalyst to provide a practical minimum of 2-MBF content varied, but it was possible in each instance to obtain a product which on distillation was improved in respect to colour on chlorination.

#### EXAMPLE 5

The phenol base product described in Example 1 as obtained by steam distillation of the crude phenol fraction and containing about 10 p.p.m. of 2-MBF was heated at 120° C. with 0.4% by weight of platinum chloride. The 2-MBF content reached a maximum of 540 p.p.m. after 6.5 hours, then began decreasing, reaching a value of about 200 p.p.m. after 54.5 hours. The addition of a further quantity of the catalyst, 1% by weight, and raising the temperature to 180° C. provided a phenol product containing about 30 p.p.m. of 2-MBF. This product on distillation gave a phenol which had a satisfactory colour on chlorination. Comparable results were obtained using palladium chloride as catalyst.

British Patent No. 865,677 claims a process for the purification of phenol derived from cumene and containing colour forming impurities including aliphatic  $\alpha$ -hydroxy carbonyl compounds which comprises subjecting the impure phenol at an elevated temperature to conditions which will cause the substantially complete condensation of the aliphatic  $\alpha$ -hydroxy carbonyl compounds with phenol to form benzofurans, and separating the phenol substantially completely from the benzofurans.

Specifically this patent claims condensation of phenol with the  $\alpha$ -hydroxy carbonyl compounds to form benzofurans in the presence of catalysts which may be activated alumina, an aluminium silicate, an acidic or basic ion-exchange resin, a mineral acid, a strong organic acid or a surface-active earth, and at a temperature between 100° and 182° C. atmospheric pressure.

#### WHAT WE CLAIM IS:—

1. The process for the purification of phenol derived from cumene which comprises subjecting the impure phenol to fractional distillation to remove acetone, heating the substantially acetone-free phenol-containing material under acid conditions with an acid catalyst until the benzofuran content of the reaction mixture has been reduced to a practical minimum, and subjecting the reaction mixture to fractional distillation to recover a purified phenol-containing material.
2. The process as claimed in Claim 1 in

which the phenol to be purified has been freed of low-boiling impurities and/or high-boiling impurities before being subjected to catalytic treatment.

5. 3. The process as claimed in Claim 1 or Claim 2 in which the catalyst is sulphuric acid, phosphoric acid, p-toluenesulphuric acid, benzenesulphonic acid or trichloroacetic acid.

4. The process as claimed in Claims 1 or 10 Claim 2 in which the catalyst is an acidic clay.

5. The process as claimed in Claim 1 or Claim 2 in which the catalyst is a halide, sulphate or nitrate of copper, chromium, mercury, platinum, zinc, cadmium, gallium, vanadium or a metal of Group IV or VIII of the Periodic Table having an atomic number less than 52.

6. The process as claimed in Claim 1 or 20 Claim 2 in which the catalyst is boron trifluoride.

7. The process as claimed in Claim 5 in which the catalyst is a Friedel-Crafts catalyst.

8. The process as claimed in Claim 7 25 in which the catalyst is ferric chloride.

9. The process as claimed in any preceding claim in which the phenol-containing material is heated in the presence of between 0.005% and 5% by weight of the catalyst based on the weight of phenol present.

10. The process as claimed in any preceding claim in which the phenol-containing material is heated in the presence of between 30 35 0.1% and 1% by weight of the catalyst based on the weight of phenol present.

11. The process as claimed in any preceding claim in which the catalytic treatment is continued until the benzofuran content of the phenol has reached a practical minimum, as determined by analysis. 40

12. The process as claimed in any preceding claim in which the treatment is carried out at a temperature between 40° and 182° C. 45

13. The process as claimed in any preceding claim in which the treatment is carried out at a temperature between 150° C. and the boiling point of phenol under the reaction pressure. 50

14. The process as claimed in Claim 13 in which the treatment is carried out under a pressure above that of the atmosphere. 55

15. The process as claimed in any preceding claim in which the treatment with catalyst is carried out under substantially anhydrous conditions. 60

16. The process as claimed in any preceding claim in which the impure phenol is treated with a base according to the process of British Patent Application Serial Number 883,746 and fractionally distilled to remove reaction products from the phenol before being heated in the presence of the catalyst. 65

17. The process for the purification of phenol as described in any of the examples herein.

18. Phenol, whenever purified by the process of any of the preceding claims.

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